The Johns Hopkins University

Visible and Infra-Red Radiation of Hydrogen

DISSERTATION
SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

By

FREDERICK SUMMER BRACKETT

BALTIMORE
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ABSTRACT

Infra-red spectrum of hydrogen to 4.5 μ.—The radiation from the central section of a long discharge tube, such as the one used by Wood to extend the Balmer series to the twentieth term, was analyzed by means of a rock-salt prism spectrometer, and readings were taken with an extremely sensitive vacuum thermo-junction. Besides some unidentified lines (Fig. 1), *five members of the Paschen series*, three of them new, were observed at the wave-lengths corresponding to the formula $\nu = N(1/3^2 - 1/m^2)$, where $m = 4, 5, 6, 7, 8$; also the *first two members of a new series* corresponding to $\nu = N(1/4^2 - 1/m^2)$, where $m = 5, 6$, were observed at 4.05 and 2.63 μ. According to the Bohr theory these two series are due to electrons falling from outer orbits into the third orbit and fourth orbit respectively.

Variation of the relative intensity of Balmer and Paschen series lines of hydrogen with the current.—For the long discharge tube used, the first Paschen line was found to increase in intensity more rapidly than Hα, as the current was increased from one-ninth to one-half ampere through a section 7 mm in diameter.

INTRODUCTION

Two lines due to hydrogen were observed by Paschen[1] at the wave-lengths 18,751 A and 12,818 A. According to the Bohr theory these are due to an electron falling into the third from the fourth and fifth stable orbits in the hydrogen atom.

In view of the very low intensities of these spectral lines observed by Paschen, the detection of a series due to an electron falling into the fourth from orbits of greater quantum number has been considered improbable. In fact the lines mentioned above, forming the first two members of the Paschen series, were so faint that in order to observe them Paschen found it necessary to set the spectrograph in the correct position according to the wave-length predicted by Ritz in consequence of his combination principle.

By using a very long hydrogen tube Professor Wood[2] found it possible to abolish the secondary spectrum from the central position of the tube, and photograph the lines of the Balmer series down to the twentieth member. From the standpoint of the Bohr theory, this increase in the intensity of the higher members of the

[1] *Annalen der Physik*, **27**, 537, 1908.

[2] *Proceedings of the Royal Society*, **97**, 455, 1920; *Philosophical Magazine*, **42**, 729, 1921.

Balmer series might be attributed to increasing the probability of transitions between the orbits of higher quantum numbers. That being the case, we should expect an increase in the intensity of lines of other series which are also due to transitions of the electron between orbits of higher quantum numbers.

That this proved to be the case, and to a degree far greater than anticipated, is the essential feature underlying the success of the present investigation.

APPARATUS

The hydrogen tube of pyrex glass, used as the source, was about one meter in length. A central portion 25 cm long was viewed end on through an elbow in the tube. This portion of the tube was 7 mm in diameter (inside dimension). This small-size tubing was also used for a distance of about 10 cm on either side of the portion viewed. The remainder of the tube was made of larger diameter in order to reduce the resistance as much as possible. The electrodes were of thin aluminum foil rolled into hollow cylinders 8 cm long by 2 cm in diameter.

Hydrogen was introduced through a capillary sealed in near one electrode. The tube was exhausted by a Gaede mercury pump, communicating with the tube near the other electrode. During observation the pump was run continuously, the pressure depending upon the balance between the pump and the capillary intake.

Alternating high potential was supplied by a 6600-volt 5-kilowatt transformer operating on a 110-volt, 60-cycle primary circuit. The potential difference applied across the tube was varied by introducing resistance into the primary. The highest current maintained through the tube was a little more than half an ampere.

The dark space about the electrodes was about 3 mm in length, the positive column occupying almost the entire length of the tube. Striation appeared only in the portions of the tube of larger diameter, the central constricted portion being occupied by apparently continuous luminosity. The secondary spectrum was noticeable only near the electrodes. Throughout the greater part of the

tube, the Balmer lines appeared with great brilliancy against a practically black background when the tube was viewed through a direct-vision prism.

The dispersion apparatus was a rock-salt monochromator of the Wadsworth type. Concave mirrors of 60-cm focal length were used for both collimator and telescope. The clear aperture of the prism was about 4 cm in diameter. Light only traversed the prism once, the simple form of apparatus being chosen in order to avoid scattered light. The slit widths were about 1 mm.

The detecting apparatus consisted of a single-junction vacuum thermo-couple, of the type constructed and previously used by Professor Pfund for measurement of stellar radiation. This was connected in series with a d'Arsonval galvonometer of sensibility about 5×10^{-10}.

A scale-distance of three meters was used, giving altogether an arrangement of extreme sensibility.

The light from the second slit was concentrated upon the blackened strip of the thermo-junction by means of a short-focus concave mirror. Both mirror and thermo-junction were protected by an asbestos housing. The leads to the galvanometer were carried through a metal conduit, grounded to prevent electrostatic effects. The galvanometer case, posts, etc., were heavily covered with cotton batting. The stability of this arrangement proved very satisfactory, deflections being reliable to 0.1 mm.

RESULTS

Part I. Distribution of intensity.—Figure 1 shows the distribution of intensity of radiation due to hydrogen in the infra-red between wave-lengths 0.5 μ and 4.5 μ.

In this diagram intensities have been plotted as the ordinates measured in millimeters of deflection of the galvanometer. It has been shown that intensities are proportional to galvanometer deflections for this thermo-couple for small deflections such as are obtained here. The abscissae are simply micrometer turns of the monochromator. The dispersion-curve based on five known points of the monochromator is shown superposed. Its ordinates

are wave-lengths in microns indicated on the right. In order to read the wave-length of any point on the intensity-curve it is

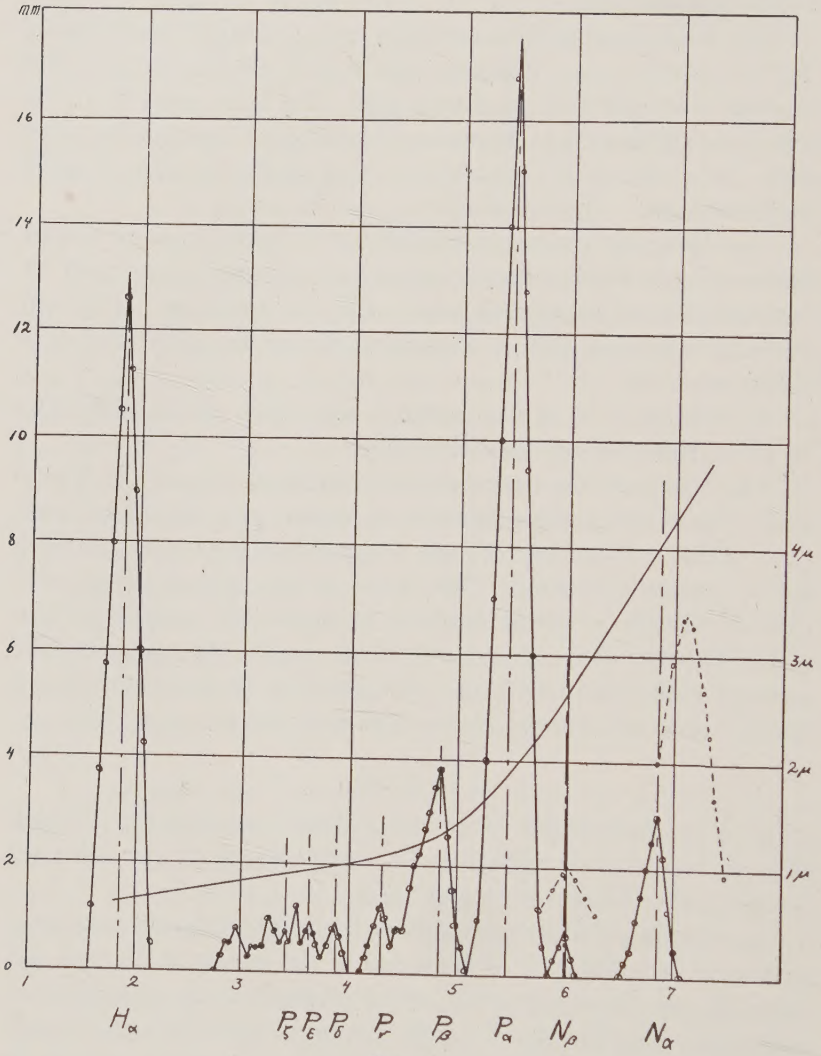

FIG. 1

merely necessary to find the point of the dispersion-curve having the same abscissa and read its ordinate at the right.

The maximum occurring at $4.05 \pm .03\ \mu$ and the second one at $2.63 \pm .02\ \mu$ are the first two members of a new series predicted from the Bohr theory by the formula

$$1/\lambda = 109{,}677.7\ (1/4^2 - 1/m^2);\ m = 5.6.$$

That is, they are attributed to an electron falling into the fourth from the fifth and sixth stable orbits of the hydrogen atom according to Bohr's model.

The largest maximum occurring at $1.88\ \mu$ is the first line of the Paschen series. It will be noted that it has an intensity greater than Hα (the last maximum on the left) in the ratio of about 4 to 3. The next four maxima are the next four members of the Paschen series.

The identity of the succeeding maxima is uncertain. Other lines are certainly present which do not belong to the Paschen series. The second maximum is probably Pζ.

These lines of the Paschen series are predicted from the Bohr theory by the formula

$$1/\lambda = 109{,}677.7\ (1/3^2 - 1/m^2);\ m = 4,\ 5,\ 6,\ 7,\ 8,\ (9),\ 10.$$

Line	Observed Wave-Length	Calculated Wave-Length
Pα	(1.88 μ)	1.875 μ
Pβ	(1.28 μ)	1.282 μ
Pν	$1.09 \pm .01\ \mu$	1.094 μ
Pδ	$1.01 \pm .01\ \mu$	1.005 μ
Pϵ	$0.95 \pm .01\ \mu$	0.955 μ

The dispersion-curve from which the wave-lengths have been determined is based upon five known points: $4.4\ \mu$ and $2.7\ \mu$ of the Bunsen flame (shown by dotted lines—scale reduced 100 times) and the three known hydrogen lines Pα, Pβ, and Hα. The values thus obtained should be quite satisfactory for purposes of identification, but of course have no great value from the standpoint of accurate wave-length measurement.

In view of the great intensity of the Paschen lines it is not surprising that many lines were readily observed which under ordinary conditions of excitation would not be detected. The

readings shown on Figure 1 were taken in sequence, without setting upon known wave-lengths. The identity of the maxima was not realized until the dispersion-curve was later plotted.

Part II. Variation of intensity with current.—As it was noticed that the appearance of the tube changed decidedly with change in current, a set of intensity readings was taken on the first lines of three series—the Balmer, the Paschen, and the new series, when the current through the tube was varied from one-sixth of an ampere to over one-half an ampere. The curves obtained are shown in Figure 2.

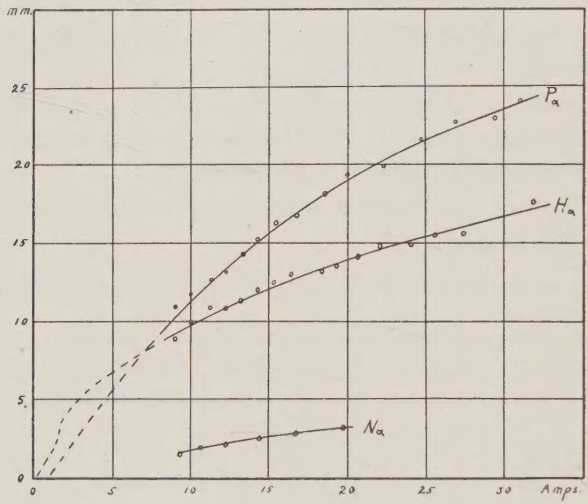

FIG. 2

The ordinates are intensities in millimeter deflections of the galvanometer, and the abscissae are current strengths through the primary of the transformer. The current through the tube is found with sufficient accuracy by dividing by 60. Readings on a of the new series are not shown for currents greater than 20 amperes primary, one-third ampere secondary, as radiation from the glass tube itself rendered them uncertain. No such effect was observed for lower currents or wave-lengths less than 3.5 μ. As a further precaution the tube was run only during the time of actual reading.

From this diagram, Figure 2, it will be noticed that although all three lines increase in intensity with increasing current, Pα increases by far the most rapidly. Further readings (dotted portion of the curve) showed that at currents less than 7 amperes primary (about one-ninth ampere secondary) Hα was more intense than Pα.

At a current of 23 amperes through the primary we have the ratio of the intensity of Pα to Hα a little more than 4 to 3. According to the Bohr theory the energy lost by an electron undergoing transition from the fourth to the third orbit of the hydrogen atom will be

$$W_{P\alpha}=(1/3^2-1/4^2)\,Nh=7/144\,Nh,$$

while that lost in transition from the third to the second orbit would be

$$W_{H\alpha}=(1/2^2-1/3^2)\,Nh=20/144\,Nh,$$
$$W_{P\alpha}/W_{H\alpha}=7/20.$$

So the energy given out by an electron in transition from the fourth to the third orbit is only seven-twentieths of that given out by an electron falling from the third to the second orbit. Hence, in order to have Pα more intense than Hα in the ratio 4:3, there must be more atoms radiating Pα than Hα in the ratio of

$$\frac{4\times 20}{3\times 7}=\frac{80}{21}.$$

In view of the greater stability of the orbits of smaller quantum number and taking into account the principle of selection, we see that this is incompatible with what would be expected if radiation were resulting only from recombination of the atom and electron after ionization. We must therefore conclude that to a large extent radiation in such a long hydrogen tube arises from inelastic collision without ionization. In such a case we may have an abnormal concentration of energy in certain wave-lengths which would not be the case for recombination after ionization, inasmuch as the probability of an electron stopping in an orbit of high quantum number is much greater, where it is simply ejected to that orbit or one of slightly greater quantum number, than in the case where it

is returning from ∞. This no doubt explains to a large extent the peculiar characteristics of the "long hydrogen tube," both in regard to the unusual intensity of the infra-red lines and also the higher members of the Balmer series.

All atoms which contribute to the radiation of the first Paschen line are left necessarily with the electron in the third orbit, whence it must proceed either to the second or the first orbit unless it is ejected to some orbit of greater quantum number by inelastic collision. Since considerably less than one-fourth of these atoms contribute to the radiation of Hα, we must conclude either that the second member of the Lyman series is radiated with great intensity, or that there must be multiple collisions to a large extent in such a tube.

It should be noticed that the higher members of the Paschen series occur in a region readily studied by photographic methods, plates hypersensitized by means of dicyanin being sensitive to 1.0 μ. This work will be carried out in the near future.

CONCLUSION

1. The first two lines of a new series have been observed at wave-lengths $4.05 \pm .03$ μ and $2.63 \pm .02$ μ, due, according to Bohr's theory, to an electron falling into the fourth from the fifth and sixth rings of the hydrogen atom.

2. Three and probably four additional members of the Paschen series have been observed.

3. The first Paschen line is more intense than Hα in the ratio 4:3 under the conditions prevailing in the long tube for great current densities.

In this work I have been much indebted to Dr. Pfund, who proposed the problem and constructed the thermo-junction, the remarkable sensibility of which rendered the work possible.

It gives me great pleasure to express my appreciation to him, to Professor Wood for his interest and many suggestions, and to Dr. Ames for his generous support.

JOHNS HOPKINS UNIVERSITY
June 1922

BIOGRAPHICAL NOTE

Frederick Summer Brackett, son of Frank Parkhurst and Lucretia (Burdick) Brackett, was born August 1, 1896, in Claremont, California. His preliminary education was obtained in the Claremont public schools. He graduated from the high school in 1910, entering Pomona College the following fall, where he pursued the general course, majoring in physics and mathematics. He was elected to Phi Beta Kappa in the spring of his Junior year. He graduated *cum laude* in February, 1918, receiving the B.A. degree *in absentia*.

He was laboratory assistant in the optical section of the Bureau of Standards for the year 1918–19, at the same time pursuing courses in advanced physics and mathematics given by Professor Ames. He was a solar observer on the staff of Mt. Wilson Solar Observatory during 1919–20, the published results of his research being *An Examination of the Infra-Red Spectrum of the Sun* λ *8900 to* λ *9900* $A°$.

He was appointed instructor in physics at the Johns Hopkins University in the fall of 1920. While there during the following two years he pursued graduate courses in physics, mathematical physics, and dynamical geology under Professors Ames, Murnaghan, and Reid.

He was an assistant physicist at the Bureau of Standards during the summer of 1920, being retained through the winter in a consulting capacity.